Patented June 6, 1944

2,350,746

UNITED STATES PATENT OFFICE

2,350,746

MINERAL OIL COMPOSITION

Everett W. Fuller, Woodbury, N. J., assignor to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

No Drawing. Application November 26, 1941, Serial No. 420,465

4 Claims. (Cl. 252—45)

This invention relates in a general way to the stabilization of viscous mineral oil fractions against the deleterious effects of oxidation or deterioration with use through the agency of oxidation inhibitors. More specifically, the present invention is concerned with the improvement of viscous mineral oil fractions by use of novel compounds, or a novel class of compounds, which when admixed with a viscous mineral oil in minor proportions will prevent or delay undesirable changes taking place in the oil. The invention is particularly concerned with the production of mineral oil compositions adapted for use in turbines and transformers.

As is well known to those familiar with the art, substantially all the various fractions obtained from mineral oils and refined for their various uses are susceptible to oxidation. The susceptibility of an oil fraction to oxidation and the manner in which oxidation manifests itself within the oil varies with the type and degree of refinement to which the oil has been subjected and with the conditions under which it is used or tested. Thus, the products formed in an oil fraction as a result of oxidation and the degree to which they are formed depends upon the extent to which the various unstable constituents or constituents which may act as oxidation catalysts have been removed by refining operations, and also upon the conditions of use.

A highly refined viscous oil, for example, which is one that has been refined by treatment with fuming sulfuric acid or other means or combinations such as $AlCl_3$, solvents and acids (or with large quantities of concentrated sulfuric acid), tends to form relatively large amounts of acidic constitutents when subjected to oxidizing conditions. The presence of catalytic materials such as copper does not appear to affect appreciably the oxidation of highly refined oils, and such oils are less prone to the formation of colored bodies or of insoluble sludge than are moderately refined oils or solvent refined oils. The formation of acidic bodies, however, is highly undesirable for most applications of these oils. For example, when used as an insulating or cooling oil in electrical equipment such as transformers or capacitors an increase in acidic bodies tends to lower the dielectric strength of the oil and has other harmful effects which are undesirable. The acids are corrosive to metals and thus reduce the useful life of the oils as lubricants or for other purposes in which they come in contact with metals, and the acidic materials are also injurious in textile lubricants and in spray oils.

Moderately refined oils, that is, oils that have been refined by treatment with only moderate amounts of sulfuric acid, or other refining agents, will form substantial quantities of insoluble sludge when used in turbines and electrical transformers. Such sludge formation clogs the pipes and vents in the oil circulation system of a turbine and the cooling ducts of a transformer. By forming films on the insulation, it reduces the heat transfer in electrical transformers and in addition it substantially reduces the dielectric properties of the oil. The changes taking place in these oils are appreciably accelerated by the presence of metal catalysts such as copper. Not only do they form considerable amounts of insoluble sludge, but they undergo material color formations and form sufficient acid to cause some reduction in the dielectric strength of these oils when in the presence of metal catalysts.

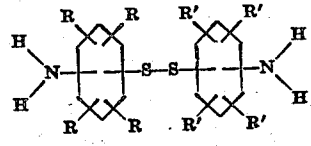
Solvent refined oils in general, which have been prepared by treatment with selective solvents, such as chlorex, phenol, furfural, etc., resemble the moderately refined acid-treated oils in that their oxidation is accelerated by the presence of metals such as copper and further in that it is attended by substantial color depreciation and sludge formation. Acid formation is usually greater than in the case of moderately acid-refined oils, but considerably less than with highly refined oils. Both sludge and acid formation lower their value for many purposes, such as electric insulation, lubrication, etc. Also, solvent-refined oils have found extensive use as lubricants for internal combustion engines because of their high viscosity index, but under the conditions of use encountered in crank cases such oils develop constituents which are corrosive toward certain metal bearings such as the cadmium-silver bearings, etc., which are sometimes used.

The high cost, as a result of high treating losses and the large quantities of refining agents used, of the highly refined oils has been responsible for the investigation of means by which oil fractions moderately refined and solvent refined to meet turbine and transformer specifications might be further enhanced by the addition of a characterizing agent thereto. Such an agent would act as a negative catalyst or inhibitor to retard the formation of sludge, acid and color bodies under the aforesaid conditions of use. As a result of these investigations, numerous compounds have been proposed for use

as inhibitors of such formations in moderately refined oils and solvent refined oils. For one reason or another, many of the compounds of the prior art are not entirely satisfactory. Among such compounds is aniline disulfide. The use of aniline disulfide, for example, is limited because of its low solubility in mineral oil fractions. Its solubility is only about 0.25% (by weight) at room temperature and it is much less than this at lower temperatures. Thus an oil containing a suitable amount of aniline disulfide for use at normal temperatures may show a precipitate of the inhibitor if it is subjected to subnormal temperatures. Also, solutions of aniline disulfide in mineral oils are only moderately stable to light and on prolonged exposure to light they tend to cloud and later to show an increasingly heavy precipitate.

As aforesaid, one object of this invention is the production of improved mineral oil fractions stabilized against the deleterious effects of oxidation upon said fractions by the addition thereto of a compound which possesses outstanding qualities as a negative catalyst or inhibitor. A further object of this invention is the production of an inhibited mineral oil composition comprising such an inhibitor and a moderately refined oil or solvent refined oil that normally tends to form considerable sludge, and some acid and color bodies, under the conditions of use encountered in turbines and transformers.

The present invention is predicated upon the discovery that alkylated diamino diphenyl disulfides represented by the general formula



wherein, R and R′ are selected from the group consisting of hydrogen and alkyl radicals, at least one R and at least one R′ always being an alkyl radical, are highly effective in small amounts in mineral oils in accomplishing the foregoing results.

The carbon-alkylated (C-alkylated) diamino diphenyl disulfides, of the type contemplated herein, are inexpensive to prepare and are readily soluble in viscous mineral oil fractions. Their increased solubility makes them superior to aniline disulfide. In addition to increased solubility, the alkylated compounds contemplated herein produce oil blends which are surprisingly superior to aniline disulfide in color stability when exposed to light. As a further improvement over oil blends containing aniline disulfide, the oil blends containing the C-alkylated compounds contemplated herein are stable against the development of a cloud in the oil at subnormal temperatures. The formation of a cloud depends upon the concentration used, the cooling temperature and the cooling cycle. The much greater oil solubility of these new compounds makes them much less liable to cloud on cooling.

Alkyl diamino diphenyl disulfides contemplated herein are readily prepared by any of the standard methods described in the literature. Thus, an alkylated nitro chlorbenzene may be reacted with sodium disulfide, and then the nitro groups reduced to amino groups, as given in the following illustrative example of the preparation of 4,4′-di-tertiarybutyl-2,2′-diamino-diphenyl-disulfide.

Example

A solution of sodium disulfide was formed by dissolving 5.3 grams of $Na_2S.9H_2O$ and 0.7 gram of sulphur in 50 c. c. of ethyl alcohol. This solution was added to 6.0 grams of 2-nitro-4-p-tertiary butyl chlor benzene dissolved in 50 c. c. of ethyl alcohol. The mixture was refluxed for one hour, then cooled and poured into 500 c. c. of water. The viscous oil was extracted with ethyl ether, washed with water, dried over anhydrous sodium sulphate, and the solvent distilled off. This left 4,4′-di-tertiarybutyl-2,2′-dinitro-diphenyl disulphide, which was reduced to the corresponding amino compound. To a mixture of 9.6 grams of iron powder and 65 c. c. of water containing 0.6 c. c. of glacial acetic acid were added 4.0 grams of the dinitro compound, and the resulting mixture warmed to 80–90° C. for 10 hours. The reaction mixture was then extracted with benzene and the benzene extract washed with water, dried, and the solvent removed by distillation. The product was further purified by dissolving it in dilute acid, filtering, and reprecipitating by adding an alkali. The 4,4′-ditertiarybutyl-2,2′-diamino diphenyl disulphide thus obtained on analysis showed:

	Found	Theory
Per cent sulphur	17.62	17.77
Per cent nitrogen	7.82	7.77

The following test examples illustrate the effectiveness of the class of compounds and certain specific members within the class contemplated herein as inhibitors for mineral oil fractions.

Test No. I

Highly refined oils

The oil used in this test was one suitable for use in transformers and had been prepared by treating a Coastal distillate with 40 pounds of 98% sulphuric acid and 180 pounds of 103% oleum per barrel, followed by washing and clay percolation. It had a specific gravity of 0.871, a flash point of 310° F., and a Saybolt Universal viscosity of 69 secs. at 100° F. This type of oil tends to form acidic products on oxidation. It was tested by heating samples to 120° C. and bubbling oxygen therethrough for a period of 70 hours. The acids thus formed were removed by titrating with alcoholic potassium hydroxide, the acidity being indicated by the so-called neutralization number (N. N.), which is the amount in milligrams of KOH required to neutralize the acids formed in one gram of the oil. The results of this test on the oil and oil blend are given in Table I below.

Table I

Compound added	Per cent used	N. N.
None		25.0
4,4′-di-tertiarybutyl-2,2′-diamino-diphenyl disulfide	0.10	0.01

Test No. II

Moderately refined oils

The oil used in this test was a mixture of Mid-Continent and Coastal distillates which had been refined by treatment with 70 pounds of 98% sulphuric acid per barrel, neutralized, washed, and

percolated through clay. It had a specific gravity of 0.879, a flash point of 383° F. and a Saybolt Universal viscosity of 152 secs. at 100° F. This is an oil suitable for use in turbines, and the test used involved heating 25 c. c. samples of the oil and oil blends to a temperature of 200° F. with 5 liters of air per hour passing therethrough. During the test the oil was maintained in contact with copper and iron by adding 24 inches of 18 gauge copper wire and one gram of iron granules to each sample. Also, during the test 2 c. c. of distilled water were added each day, and the samples were tested for acidity or neutralization number, color and sludge formation at varying periods of time. The results of these tests with this oil and blends of the same oil containing representative compounds of the type contemplated herein are set forth in Table II below, from which it will be observed that all of these compounds show an appreciable effect in inhibiting the deterioration of this type of oil.

Table II

Inhibitor	Per cent	Time, hrs.	N. N.	Lov. color	Sludge mg./25 c. c.
None		72	0.14	6	68
		168	0.99	25	17
		240	2.5	110	246
		336	16.0	400	1,282
4,4'-di-tertiarybutyl-2,2'-diamino diphenyl disulfide	0.05	167	0.7	23	24
		335	3.0	75	84
Do	0.10	167	0.4	40	16
		335	1.6	60	48
Do	0.20	167	0.0	55	1
		501	2.9	100	78
4,4'-diamyl-2,2'-diamino diphenyl disulfide	0.10	333	0.8	95	37
		668	4.6	110	294

TEST No. III

Solvent refined oil

The oil used in this test was a distillate from a Rodessa Crude which has been refined by solvent extraction with furfural, dewaxed and filtered. The finished oil had a specific gravity of 0.856, a flash point of 420° F., and a Saybolt Universal viscosity of 151 secs. at 100° F. It was tested by the same procedure followed in Test No. II, and the results obtained are set forth in Table III below.

Table III

Inhibitor	Per cent	Time, hrs.	N. N.	Lov. color	Sludge mg./25 c. c.
None		92	0.91	9	33
		165	20.3	320	251
4,4'-di-tertiarybutyl-2,2'-diamino diphenyl disulfide	0.10	167	0.1	1	7
		335	0.0	1	6
		1,487	0.04	7	20
Do	0.05	166	0.01	2	2
		501	5.3	9	57
4,4'-diamyl-2,2'-diamino diphenyl disulfide	0.10	333	0.01	6	11
		668	0.02	11	14

It will be observed from the foregoing tabulated results that the alkylated diamino diphenyl disulfides when used in small amounts in mineral oil fractions potentially susceptible to the formation of sludge, acid, and color bodies, are highly effective inhibitors of said formation.

As aforesaid, one important and surprising advantage of the C-alkylated diamino diphenyl disulfides over the unalkylated compound (diamino diphenyl disulfide or aniline disulfide) resides in the greater light stability of oils containing the former compounds of the present application, over oils containing the aniline dissulfide of the prior art. This is demonstrated by the fact that on exposure to ordinary room light an oil containing 0.1% of diamino diphenyl disulfide became cloudy within 14 days and showed an appreciable precipitate by 122 days; whereas, the same oil containing 0.1% of a C-alkylated diamino diphenyl disulfide (4,4'-tertiarybutyl-2,2'-diamino diphenyl disulfide) was only slightly cloudy after 48 days and showed only a very slight trace of a precipitate in 122 days.

It is to be understood that the terms "highly refined," "moderately refined" and "solvent refined" as used herein have reference to oils corresponding substantially in their manner of deterioration and inhibitor response to the examples given and are not necessarily restricted to oils obtained by particular refining operations. As has been previously pointed out, the final characteristics in an oil fraction are effected by the crude from which the oil is obtained as well as the refining treatment, and by selection of the crude stock, an oil of the "highly refined" type may be obtained by a treatment which on another crude stock would yield an oil having the characteristics of a "moderately refined" oil.

The amount of the inhibitor used may be varied, depending upon the oil fraction and use to which it is put, from about 0.01% to about 1.0%. In general, the amount satisfactory for substantial inhibition will be of the order of from about 0.05% to about 0.5%.

I claim:

1. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion of 4,4'-di-tertiarybutyl-2,2'-diamino diphenyl disulfide in an amount sufficient to inhibit the deleterious effects of oxidation upon the oil.

2. A mineral oil composition of the type adapted for use in turbines and transformers comprising a moderately refined mineral oil potentially susceptible to the formation of sludge under the conditions of use normally encountered in turbines and transformers, and a minor proportion of 4,4'-di-tertiarybutyl-2,2'-diamino diphenyl disulfide in an amount sufficient to resist the formation of said sludge under said conditions of use.

3. An improved mineral oil composition comprising a viscous mineral oil fraction and in admixture therewith a minor proportion, sufficient to inhibit the deleterious effects of oxidation upon the oil, of a compound selected from the group consisting of 4,4'-di-tertiarybutyl-2,2'-diamino diphenyl disulfide and 4,4'-diamyl-2,2'-diamino diphenyl disulfide.

4. A mineral oil composition of the type adapted for use in turbines and transformers comprising a moderately refined mineral oil potentially susceptible to the formation of sludge under the conditions of use normally encountered in turbines and transformers, and a minor proportion, sufficient to resist the formation of said sludge under said conditions of use, of a compound selected from the group consisting of 4,4'-di-tertiarybutyl-2,2'-diamino diphenyl disulfide and 4,4'-diamyl-2,2'-diamino diphenyl disulfide.

EVERETT W. FULLER.